

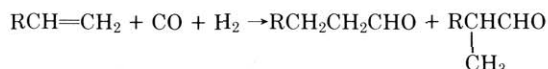
Hydroformylation

An Old Yet New Industrial Route to Alcohols

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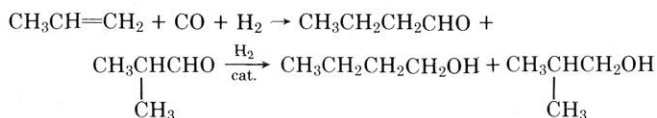
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The hydroformylation reaction (also known as Oxo) consists of the addition of carbon monoxide and hydrogen to an olefin to form an aldehyde and, in some cases, an alcohol (1).



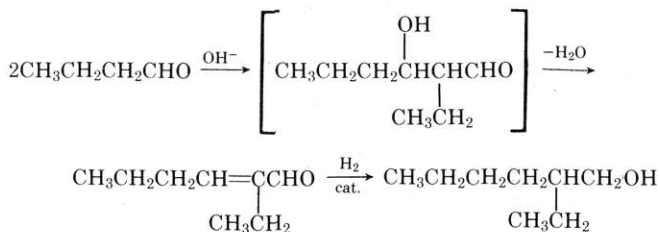
It was discovered by Otto Roelen in Germany and has been commercially utilized in the United States since the immediate post-World War II period. Its use has grown steadily, and it has displaced other successful technology, such as the ethylene-to-acetaldehyde-to-butyraldehyde synthesis. This success has been due largely to the availability of inexpensive raw materials, in particular propylene and synthesis gas. Synthesis gas has been produced on a large scale for many years as a source of hydrogen for ammonia and for methanol production. It in turn is manufactured principally by reforming of methane, although other processes involving heavy oil residuum partial oxidation and coal gasification have been commercialized in recent years.

Aldehydes are intermediates for a variety of chemicals: amines, acids, and especially alcohols. By the nature of the reaction pathway, only *primary* alcohols are produced.



Aldehydes are produced ranging in carbon number from propionaldehyde to detergent range, C_{12} – C_{15} . The largest volume single products are butanol and 2-ethylhexanol, with U. S. capacities of 1,595 (2) and 770 (3) million lbs/y, respectively.

Both butanol and 2-ethylhexanol are based on propylene as the base hydrocarbon feedstock. The detergent-range alcohols are based on ethylene. An example is the SHOP process of Shell Oil Co., which uses a combination of ethylene oligomerization, olefin isomerization, and metathesis to produce C_{10} – C_{20} α -olefins and C_{11} – C_{14} internal olefins (4).



This route allows alcohols of high linearity, and the detergent products are more biodegradable than the corresponding branched detergents. Linear alcohols in the general plasticizer range (C_7 – C_{11}) are also produced from ethylene-based oligomers (C_6 , C_8 , C_{10} α -olefins), but the amounts are less than 2-ethylhexanol.

Exxon Chemical produces alcohols in the C_6 – C_{13} range from C_5 – C_{12} olefins, based on mainly propylene as the feedstock. These alcohols are primarily methyl branched, with phthalate ester plasticizers as the major products.

Catalysts and Ligands

Cobalt

All earlier Oxo processes utilized cobalt as the catalytic Group VIII metal. Under reaction conditions (140–175°C, 20–30 MPa) the actual catalyst is tetracarbonyl cobalt hydride, $\text{HCo}(\text{CO})_4$. It may be generated *in situ* from the reaction of carbon monoxide and hydrogen with cobalt salts of organic acids. The carbonyl hydride is unstable and easily decomposes with the formation of cobalt metal. The high pressure of carbon monoxide is necessary to ensure against decomposition within the reactor. The cobalt carbonyl must be removed from the product and recycled for further catalysis. Several methods have been devised to accomplish this objective, indeed a large portion of the patent literature of the 1950–70 decades was devoted to this subject. By one procedure or another, the cobalt is extracted and converted back to cobalt salts for reintroduction into the reactor.

A simplified mechanistic scheme for cobalt catalysis is shown in Figure 1. This will be used as basis for discussion for other catalyst systems as well as for unmodified cobalt. The scheme depicts the pathways for both linear and branched α -olefins. It does not include internal or cyclic olefins or other isomers that are obtained via simultaneous isomerization-hydroformylation.

All of the steps in the catalytic cycle are reversible, with the possible exception of the cleavage of the acyl complex to form aldehyde (steps IVa and IVb). Steps IIa and IIb are olefin insertion into a metal-hydride bond, the reverse of these steps is β -hydride elimination to form M-H bond and olefin-metal complex. Since both the forward and reverse

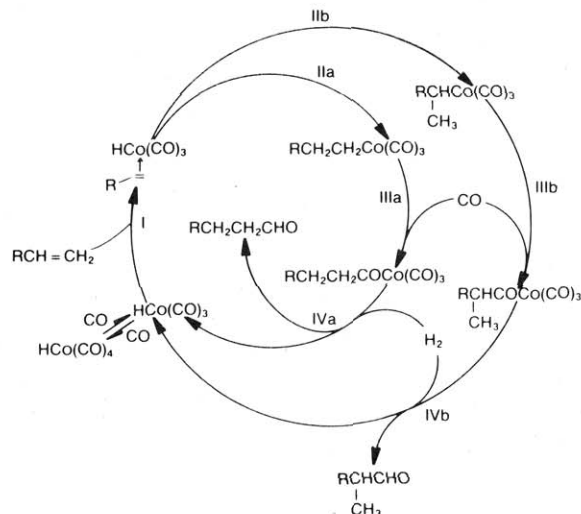
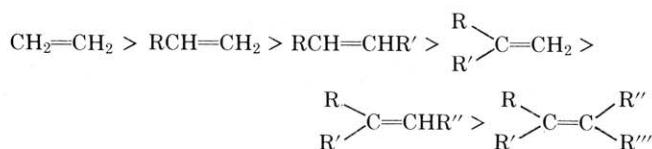


Figure 1. Hydroformylation mechanistic scheme.

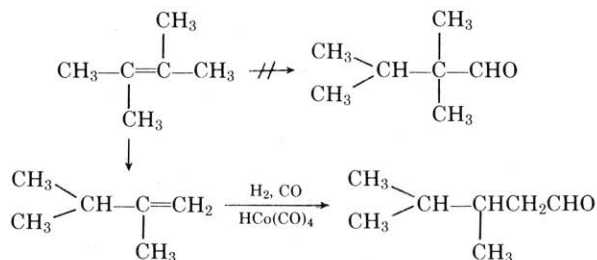
steps can occur in either of two directions, isomerization occurs to produce products other than those in which the elements of -H and -CHO have been added to the unsaturated carbon atoms as they existed in the starting olefin. Of course, this implies that the rate of isomerization (insertion-elimination) is substantially greater than the rate of "carbonyl insertion" (steps IIIa and IIIb).

The "carbonyl insertion" is actually migration of the alkyl group to the carbon atom of a metal-complexed carbon monoxide. The intermediate branched and linear acyl complexes are cleaved with addition of hydrogen to produce aldehyde and to regenerate the effective catalyst $\text{HCo}(\text{CO})_{3,4}$. This latter step is perhaps the least understood of the catalytic cycle in both the cobalt and rhodium catalyzed reactions (*vide infra*).

Olefin reactivity decreases with the degree of substitution on the olefin carbon atoms.



The tetrasubstituted olefin will not react as such. Aldehydes are not formed to any significant degree in which the α -carbon is substituted by three alkyl groups. Instead, isomerization takes place first, followed by hydroformylation of the resulting less-substituted olefin.



This ability to isomerize is important for understanding product distribution from the hydroformylation of higher olefins, in which the olefin may be terminal or internal and linear or branched. Haymore et al. (5) studied the distribution of aldehydes obtained from such C_8 olefins. Three significant sets of results are shown in Figure 2. Among the noteworthy observations are: terminal addition of -CHO is preferred to internal; all carbons are acylated, even the one at the opposite end of the chain; acylation at a branched carbon or on the internal carbon adjacent to the branching is disfavored; the difference between terminal and internal olefin is significant but not marked.

Cobalt-Phosphine

In view of the facts that *n*-butyl alcohol is preferred to isobutyl alcohol in most ester applications, that only butanal can be condensed to 2-ethylhexanol, and that linear detergents have superior biodegradable properties, much research has been directed toward increasing the linear aldehyde content of the product (*N/I* ratio). In the 1960's the Shell Oil Company commercialized a catalyst system which employs a trialkylphosphine cobalt tricarbonyl hydride. The product contains a much higher percentage of linear product, up to 90%, even from internal linear olefin. Other advantages include increased catalyst stability (the catalyst can be recycled without extraction and regeneration) and lower pressures (5–10 MPa). Disadvantages include lower reaction rates and increased hydrogenation of olefin to alkane. Substitution of a trialkylphosphine for one CO ligand on the cobalt greatly alters the electronic and steric properties of

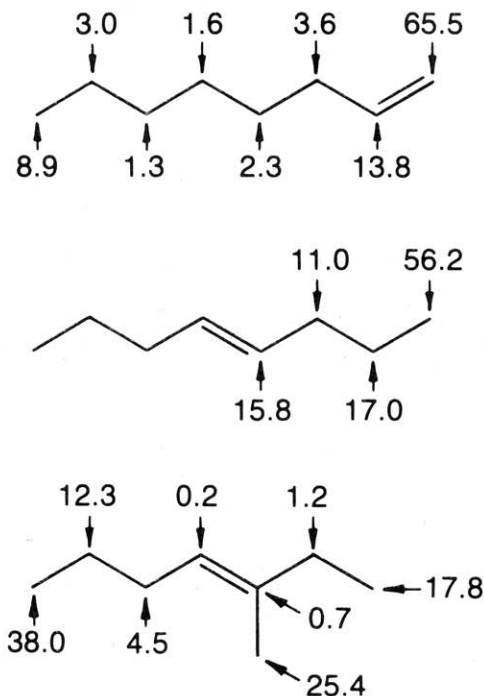


Figure 2. Product distribution from hydroformylation of octenes.

the resulting complex and alters the dual insertion pathway in favor of formation of linear alkyl cobalt carbonyl (step IIa and IIb). Also the phosphine substitution increases the relative rate of sequential hydrogenation of the aldehyde, so that the product can be principally a linear alcohol.

Rhodium-Phosphine

The newer system commercialized in the 1970's by Union Carbide employs a rhodium-triphenylphosphine catalyst, produces *N/I* ratios of 15:1, and requires low temperature and low pressure. A general comparison of the three major systems is shown in the table.

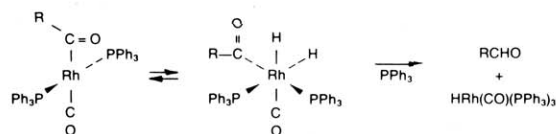
The same general catalytic pathway is believed to occur in rhodium as in cobalt hydroformylation. However, in the case of rhodium complexes, multiple substitution by triphenylphosphine occurs. This ease of substitution results in a greater ability to control the linear-branched competitive pathway in the rhodium analog of steps IIa and IIb. By varying the reaction parameters, especially the concentration of phosphine and the partial pressure of carbon monoxide, the *N/I* ratio (IIa versus IIb) can be varied at will. But since the linear products are generally more valuable, more effort has been directed toward high ratios and ratios $\geq 15:1$ are easily realized in commercial practice. It is generally accepted that the multiphosphine-substituted species exert steric control and favor linear alkyl and acyl complexes.

Another major difference between the rhodium and cobalt phosphine catalyst systems lies in the relative propensity for

Comparison of Three Major Hydroformylation Processes

	Co	Co + PR_3	Rh + PPh_3
Temp ($^{\circ}\text{C}$)	140–180	160–200	90–110
Pressure (MPa)	20–30	5–10	1–2
Hydrocarbon Formation	Low	Significant	Low
Product	Aldehyde, Alcohol	Alcohol, Aldehyde	Aldehyde
<i>N/I</i>	3–4:1	8–9:1	12–15:1

1. Oxidative Addition of Hydrogen



2. Binuclear cleavage of Acyl

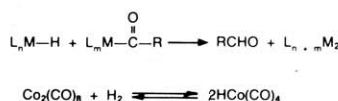


Figure 3. Postulated schemes for cleaving acyl to form aldehyde.

isomerization/hydrogenation. It has been proposed (6) that for rhodium the β -hydride elimination (steps IIa, IIb, reverse) is much slower than the alkyl migration steps (IIIa, IIIb). Thus there is to date no successful rhodium process for converting internal olefins to linear aldehydes.

In Figure 1, steps IVa and IVb are combinations of at least two steps each. Two principal pathways have been proposed for the reductive cleavage of the acyls to form aldehydes. One involves the oxidative addition of hydrogen to an unsaturated acyl complex, followed by reductive elimination of aldehyde with concomitant catalyst regeneration. The pathways are exemplified for rhodium in Figure 3.

The second pathway is a binuclear elimination of aldehyde from acyl and hydride species. It is known that dicobalt octacarbonyl is cleaved with hydrogen to produce tetracarbonyl cobalt hydride and that the mononuclear and dinuclear species are in equilibrium at conditions similar to those in a typical hydroformylation reaction. Evidence relative to these pathways has been published for rhodium (7) and for cobalt (8). It appears that complete resolution of the question has not yet been reached.

The expense of rhodium demands that both extremely low adventitious losses and extended catalyst life be realized. The catalyst life must be sufficient to produce at least 10^6 – 10^7 lbs of aldehyde per lb of rhodium. Catalyst life is impaired by extrinsic poisons such as strong acid, HCN, and sulfur as H_2S or COS. Feed stream purification negates this potential problem. But rhodium catalyst life is also impaired by intrinsic deactivation. This phenomenon is evident in systems which have been under hydroformylation conditions for some time (9). Recent studies have shown that the deactivation involves insertion of rhodium into a P-C bond of triphenylphosphine (10). Insertion of olefin into the metal hydride bond produces a metal alkyl complex, which reductively eliminates an alkyldiphenylphosphine. This slow conversion is detected in reacting hydroformylation solutions. The mononuclear phosphido complex can also eliminate Ph as benzene, biphenyl, etc., with concomitant formation of polynuclear species (Fig. 4). These are more coordinatively and structurally stable than their mononuclear counterparts

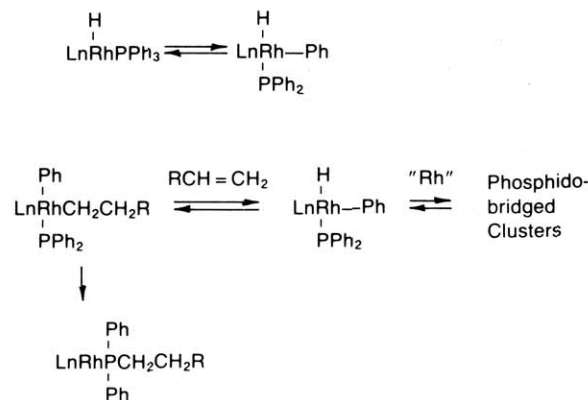


Figure 4. Proposed catalyst degradation pathway.

and possess significantly diminished catalytic activity. Conditions for minimizing the deactivation of rhodium have been correlated with the reaction parameters (9). It is interesting to note that increased olefin concentration will decrease phosphido-bridged cluster formation, but will increase alkyldiphenylphosphine formation.

New Processes

The most significant of new variants on cobalt or rhodium catalysis is the water-soluble rhodium catalyst developed by Rhone Poulenc/Ruhrchemie (11) and which is presently being used for a portion of the Ruhrchemie production at Oberhausen FRG. The ligand, trimetasulfonatotriphenylphosphine sodium salt, is extremely water soluble and maintains the rhodium catalyst in an aqueous phase. The organic phase contains reactant propylene and product butyraldehyde. Phase separation of product from catalyst is easily accomplished. *N/I* ratios of 19:1 are realized and operating conditions are mild.

It is anticipated that rhodium technology will grow in domination of hydroformylation practice. The chief barriers as originally visualized, which were mostly concerned with containment of the rhodium and maintenance of its activity, have been shown not to be cause for undue concern. Processes adapted to special cases of functional olefins and to higher olefins can be expected.

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